Application of 2-(Piperidinomethyl)-4-Methylphenol for Extraction Spectrophotometric Determination of Iron

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Abstract The optimal conditions for the extraction-spectrophotometric determination of iron with 2-(piperidinomethyl) -4-methylphenol (L) based on the Fe^{III}-L = 1: 2 complex were as follows: pH (3.8-5.2), PAR concentration (4.5×10^{-4} mol L^{-1}), extraction solvent ($CHCl_3$), shaking time (5 min), wavelength for spectrophotometric measurements (535 nm) and volumes of organic phases (5 ml of chloroform). The complexing form of iron is $FeOH^{2+}$. With a single extraction with chloroform, 98.4% of the iron is recovered as a complex. Based on the data obtained, photometric methods for determining iron in soils are developed.

Keywords iron, Fe-L complex, extraction, spectrophotometry, soils, calibration graph

Introduction

Iron belongs to transition elements and forms very strong coordination bonds with any donor ligand atoms. Since Fe^{II} and Fe^{III} ions have chromophore properties, most methods use reagents that do not contain chromophore groups [1]. 4-(2-Pyridylazo)resorcinol is one of the most popular analytical reagents. It forms colored complexes with many metal ions and can be used for their spectrophotometric determination. A well-known disadvantage of this reagent is its insufficient selectivity [2]. Selective reagents for Fe^{III} are compounds containing phenolic OH groups [1]. Reagents containing OH groups and donor nitrogen atoms are considered the most suitable for the determination of Fe^{III} [3]. For photometric determination of iron mainly they use 1,10-phenanthroline, 2,2'-dipyridyl and 2,2',2"-tripyridyl [4]. Photometric methods have been developed to determine Fe^{III} in fruits with 1-phenyl-2,3-dimethylpyrazolone-5-aziopyrogallol in the presence of 1,10-phenanthroline and α, α'-dipyridyl [4]. Earlier, we investigated the interaction of some d-elements with halogenated thiophenols and hydrophobic amines [5−6]. This work presents the results of an extraction-photometric study of the complexation of Fe^{III} with 2- (piperidinomethyl)-4-methylphenol (L).

Materials and Methods

Reagents and instruments

Stock solutions (1 mg mL^{-1}) of iron(II) and iron(III) were prepared by dissolving$(NH_4)_2SO_4 \cdot$
$FeSO_4 \cdot 6H_2O$ and $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O$ in distilled water containing H_2SO_4 [7]. Working solutions with a concentration of 2.2×10^{-4} mol L^{-1} were obtained by asuitable dilution of the standardized stock solutions with distilled water. 2- (piperidinomethyl) -4-methylphenol was synthesized according to the procedure [8]. The synthesized reagent was identified using elemental analysis, IR and NMR spectroscopy [9]. Chemical analysis

results: Found,%: 86.98 C; 3.57H; 3.68 N; 4.12 O. Calculated,%: 87.64 C; 3.93 H; 3.93 N; 4.49O.IR spectrum (KBr)- 3470 см$^{-1}$ ν (OH), 3050 см$^{-1}$ν(CH), 2850 см$^{-1}$ ν(CH$_3$), 1610–1450 см$^{-1}$ν(C$_6$H$_5$), 820-710 см$^{-1}$ δ(C-H),1480-1470 см$^{-1}$δ(-CH$_2$), 1420 см$^{-1}$ (ν$_{CN}$), 1391см$^{-1}$ (ν$_{CO}$).

^{1}H NMR spectrum (300.18 MHz, C$_6$D$_6$).2.90 (s, 3H, CH$_3$), 2.45 (s, 2H, N-CH$_2$piperidine), 1.60-2.47 (m, 10H, piperidine), 7.38–7.42 (m, 3H, Ar). We used a 0.01 M solution of L in chloroform. Purified chloroform was used as an extractant. The ionic strength of the solutions (μ = 0.1) was kept constant by introducing the calculated amount of KNO$_3$. To create the required acidity of the solutions, an acetate buffer solution (prepared by mixing 2.0 mol L^{-1} aqueous solutions of CH$_3$COOH and NH$_4$OH). The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer and KFK- 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples. TIR and NMR spectra were recorded on a spectrophotometer "Bruker" (Germany).

General procedure for the determination of iron
10-100 μg of iron is introduced into 25-mL volumetric flasks with an interval of 10 μg, 3 mL of 0.01 M solution L, the volume of the organic phase is adjusted to 5 ml with chloroform, the pH is controlled, diluted with water to the mark and the optical density of the solutions relative to water is measured. Based on the data obtained, calibration graphs are built.

Analytical procedure
An aliquot of the analyzed sample solution [light alluvial-deluvial meadow soil PS-1, COOMET No. 0001-1999BG, SOD No. 310a-98 (Soil 1); light meadow cinnamonic soil PS-2, COOMET No. 0002-1999BG, SOD No. 311a-98 (Soil 2); and light alluvial-deluvial meadow soil PS-3, COOMET No.0003- 1999 BG, SOD No. 312a-98 (Soil 3)] was placed in a separatory funnel. A2.5 mL of the Lsolution, and 3.0 mL of the buffer solution (pH 4.0) were added. The resulting solution was diluted with distilled water to a total volume of 10 mL. A 2.5 mL volume of chloroform was added and the funnel was shaken for 2 min.

Determination of the charge sign of the complex
During electrolysis of the solution of the complex, its movement was not observed either to the anode or to the cathode even after prolonged transmission of current, i.e., it is electrically neutral. The experiments were conducted in the usual way, in a U-shaped tube with two taps, at a voltage of 180-200 V and a current strength of 0.5-0.8 mA. Electrolysis was carried out for 3 hours.

Results and Discussion
Effect of pH
We used ammonium-acetate buffers to control pH. Extraction decreases both with decreasing and increasing pH of the aqueous phaseFrom Fig. 1 shows that iron (III) complexes are extracted into chloroform in the pH range 3.8-5.2. Extraction of Fe(III) enhanced with the increase inthe acidity of the initial solution; the further increase in acidity lead to the gradual decrase ofrecovery, which was obviously associated with a decrease in the concentration of the ionizedform of L. Probably, it is present in the solution in the non-dissociated state. At pH ≥ 6, the complexes were hardly extracted, canbe attributed to hydrolysis.

Choice of solvents
To clarify extraction capabilities of the complex tested non-aqueous solvents: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzol, chlorobenzol, toluene, xylene, isobutanol and isopentanol and mixtures of organic solvents.

Most effective for extraction of the complex and speed toequilibrium is chloroform, dichlorethane and four carbon chloride. For one extraction of Fe (II) is extracted with chloroform 98.4% as F-L.The iron content in the organic phase was determined photometrically - salicylic acid[2]afterreextraction, and in the aqueous phase by difference.

Figure 1: Effect of pH of the aqueous phase on the absorbance of the complex

$C_{Fe(III)} = 3.57 \times 10^{-5}$mol L^{-1}M, $C_L = 4.50 \times 10^{-4}$mol L^{-1}, $V_{aq.\ phase}$=20 mL, $V_{orq.\ phase}$ =2.5mL.
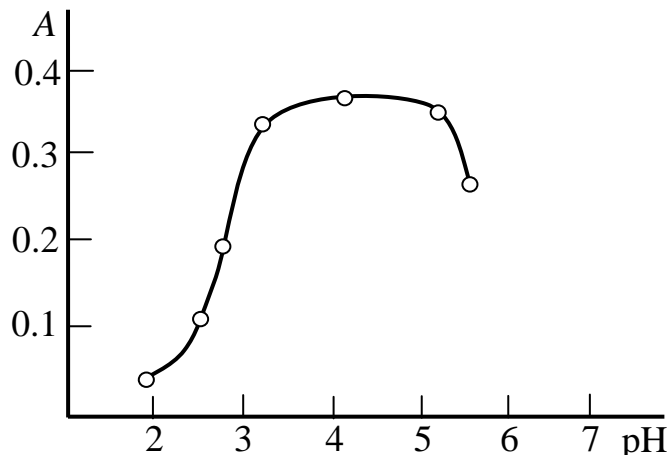
Absorption spectra

The maximum analytical signal during the complexation of iron with L is observed at 535 nm. L absorb as much as possible at 256 nm. The bathochromic shift is 279 nm. The contrast of the reactions is high: the initial reagent is almost colorless, and the complex is red-violet. The molar absorption coefficient is $\varepsilon = 3.29 \times 10^4$.

Effect of L concentration

The effect of L concentration on the absorbance is shown in Figure 2. It can be seen that the complex is stable (there is a sharp break in the saturation curve).The yield of the complex is maximum at a concentration of 3.5×10^{-4}mol L^{-1} L. We performed our further experiments with L concentration of 4.5×10^{-4}mol L^{-1}. This concentration provides sufficient L-to-Fe excess even when the solution contains foreign ions prone to form complexes with L.
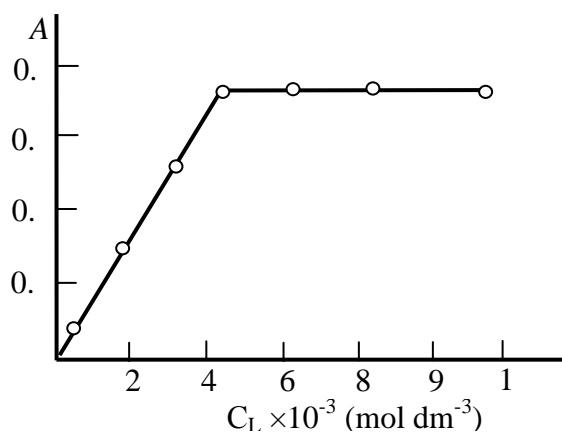

Figure 2: Effect of L concentration on absorption in chloroform

$C_{Fe(III)} = 3.57 \times 10^{-5}$mol L^{-1} M, $C_L = 4.5 \times 10^{-4}$mol L^{-1}, $V_{aq.\ phase}$=20 mL, $V_{orq.\ phase}$ =2.5mL.

The effect of shaking time
Experiments were carried out with different shaking times (Fig. 3). The results show that the iron complex with L is stable in aqueous and organic solvents and does not decompose for two days, and after extraction for more than a month. Maximum optical density is achieved within 5 minutes.
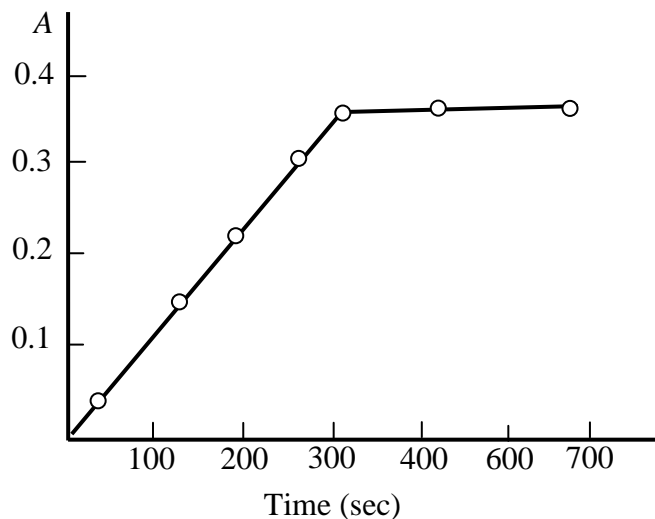

Figure 3: The effect of shaking time on the absorption of the complex
$C_{Fe(III)} = 3.57 \times 10^{-5}$ mol L^{-1} M, $C_L = 4.5 \times 10^{-4}$ mol L^{-1}, pH = 4.5, $V_{aq. phase} = 20$ mL, $V_{orq. phase} = 2.5$ mL.

The effect of the ratio of volumes of aqueous and organic phases
The course of the obtained experimental curves suggested that the increase in the volume over 110 mL is pointless. The optimum chloroform volume was 3 mL. Smaller volumes resulted in insufficient repeatability of the results. The degree of extraction does not depend on the ratio of the volumes of the aqueous and organic phases in a wide range (from 5: 5 to 110: 5), which makes it possible to simultaneously concentrate and photometrically determine iron. The concentration coefficient reaches 10.

Stoichiometry of the complexes and themechanism of complexation
It was found using the Nazarenko method that Fe(III)in the complexes was present in the form of $FeOH^{2+}$. Thenumber of protons replaced by cobalt in one L molecule appeared to be one [10]. Additional experiments by the Akhmedly's method [11] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 0.92).
The stoichiometry of the Fe(III):L complex was determined by, Asmus method,equilibrium shift method, Starik-Barbanel relative yield method and crossed lines methods [12]. It shows that thecomposition of Fe(III):L complex is 1:2 (Fig 4).
The Fe (III) complex with L was synthesized and studied by chemical analysis and IR spectroscopy. The observed disappearance of the absorption band in the region of 3600-3250 cm^{-1} with a maximum at 3470 cm^{-1} shows that -OH is involved in the formation of a bond with the metal. In the IR spectrum of the complex, the vibrational frequency νCN (1350 cm^{-1}) is shifted to the low-frequency region by 30 cm^{-1} in comparison with the IR spectrum of the free ligand (absorption band $ν_{CN} = 1850$ cm^{-1}). This suggests the coordination of the ligand to the metal through the nitrogen atom of the piperidine ring. The absorption bands at 440 cm^{-1} and 573 cm^{-1} correspond to ν (Fe − O) and ν(Fe − N), respectively [9, 13]. In the IR spectrum of the complex, the vibrational frequency $ν_{CN}$ (1390 cm^{-1}) is shifted to the low-frequency region by 30 cm^{-1} in comparison with the IR spectrum of the free ligand (absorption

band ν_{CN} = 1420 cm^{-1}). This suggests the coordination of the ligand to the metal through the nitrogen atom of the piperidine ring.

The iron content in the complexes was determined after their decomposition aqua regiaphotometrically using phenantroline. The purity of the compound was checked by the elemental analysis. Elemental analysis individually complexes are Table 1.

Table 1: Elemental analysis of ligand L and complex Fe-L

Compound	%	C	H	N	Fe
L	Found	48.51	0.45	4.49	-
	Calculated	48.97	0.68	4.76	-
Fe-L	Found	67.35	6.72	6.89	13.91
	Calculated	68.42	7.00	7.00	14.00

The stability constant of complex Fe(III)-L was calculated and found to be lgβ = 9.5 at room temperature. The sizes of equilibrium constant K ecalculated on a formula lgKe= lgD - lg[L] were presented in Table 2.

Thermogravimetric study of the complex Fe- L shown that thermal decomposition of the complex takes place in two stages: at 56-112°C water evaporates, at 420-530°C-decomposed L. The final product of the termolysis of the complex is Fe_2O_3.
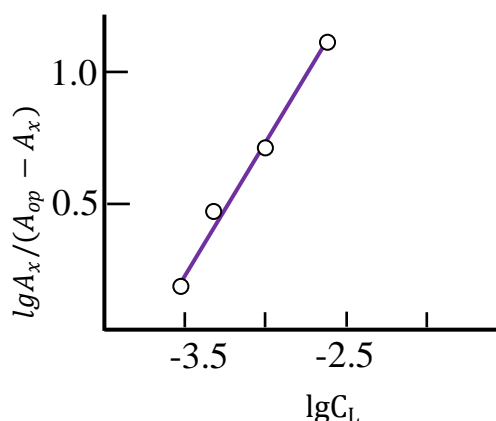

Figure 4: Determination of the ratio of components by equilibrium shift method for Fe– L.

$C_{Fe(III)}$ = 3.57×10^{-5}mol L^{-1} M, C_L= 4.50×10^{-4}mol L^{-1}, pH = 4.5, $V_{aq. phase}$ =20 mL, $V_{orq. phase}$ =2.5mL.

Table 2: Optical characteristics, precision and accuracy of the spectrophotometric determination of Fe(II) with L

Parameters	Value
Color	red
The pH range of education and extraction	1.8-6.2
The pH range of maximum extraction	3.0-5.9
λ_{max} (nm)	530
Molar absorptivity (L· mol^{-1} cm^{-1})	3.29·10^4
Sandell's sensitivity (ng·cm^{-2})	1.91
R,%	97.5
The equation of calibration curves	0.035+0.040x
Correlation coefficient	0.9975
lg K_{ex}	5.82
Stability constant (β)	9.5
Beer's law range (μg·ml^{-1})	0.2-18
Limit of detection (LOD): ng ·mL^{-1}	14
Limit of quantification (LOQ): ng ·mL^{-1}	42

Given the molar ratio of the components in the complex, the complex-forming form of the central ion, the monomer complex in the organic phase, as well as the data of IR spectroscopic, thermogravimetric and chemical analysis, the structure of the Fe (III) complex with L can be represented:
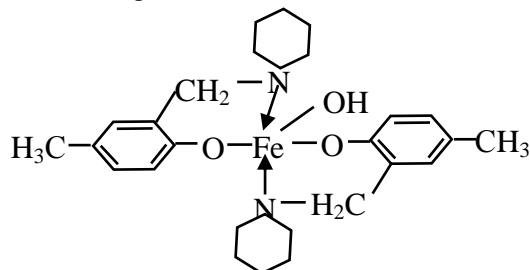
Effect of foreign ions

Various ions which are often found together with iron in natural and industrial samples were used to test the selectivity of the proposed procedure. The tolerance limit of the ions shows minimum deviation (± 2 %) in absorbance. Experiments were performed according to the recipe, by which established calibration curves, with the only difference that a solution other than Fe(II) injected a certain amount of the corresponding ions. Of the cations studied - Co^{II}, Ni^{II}, Cd^{II}, Bi^{III}, Cu^{II}, Zr^{IV}, W^{VI}, Hg^{II}, Ti^{IV}, V^{IV}, Mo^{VI}, Mn^{II}, Nb^{V}, Ta^{V}, Cd^{II}- only Mn^{II}, Co^{II}, Ni^{II} and Ag^{I}interfere . The interfering effect of Mn^{II}, Co^{II}, Ni^{II}, and Cd^{II} was eliminated by precipitation of Fe^{III} with ammonia. The interference of various cations was removed by using suitable masking agents. Interference of Zr^{IV} eliminated sodium fluoride; Cu^{II} - thiourea; Ti^{IV} - tiron or sodium fluoride; Hg^{II} ion -sulfit; Nb^{V} and Ta^{V} - oxalic acid, and Mo^{VI} and W^{VI} -sodium fluoride and oxalic acid. When using a 1%solution of ascorbic acid does not interfere withdetermination Mn^{II}, V^{IV}, Nb^{V}, Cr^{VI} andMo^{VI}. The effect of various ions and reagents on the extraction-spectrophotometric determination of 50 mg iron (II) is summarised in Table 3.

Table 3: Tolerance limits of foreign ions in determination of 50 μg of Fe^{III} by the developed procedure (*n*=6, P=0.95)

Foreign ion, FI	FI to Fe^{III} ratio tolerance limit
Co^{II}*, Ni^{II}, W^{VI}*, Mo^{VI}*, Ag^{I}*	25
Cd^{II}, Bi^{III}	200
Cu^{II}*	15
Zr^{IV}, Mn^{II}, UO_2^{2+}	50
Hg^{II}*, V^{IV}*	40
Ti^{IV}	30
Nb^{V}*,Ta^{V}*	60
NH_4^{+}, NO_3^{-},	1000
CH_3COO^{-}, J^{-}	100
F^{-}	110
SO_4^{2-}	125
$C_2O_4^{2-}$	50

Note:* The disturbing effect was eliminated by masking agents:Co^{II}- ascorbic acid; Cu^{II}- $Na_2S_2O_3$; W^{VI}-щавелевая кислота; Hg^{II}- $Na_2S_2O_3$; V^{IV}- H_2O_2; Mo^{VI} -NaF; Nb^{V} -NaF; Ta^{V}- NaF; Ag^{I}-KBr.

Beer Law and Analytical Characteristics

Following Beer's law was studied by measuring the absorption value of a number of solutions containing various concentrations of iron ions. A linear calibration graph drawn between the absorption and the concentration of iron ions shows that Fe (II) can be determined in the range of 0.2-18 μg / ml. The equations of the obtained lines and

some important characteristics regarding the use of the Fe(III)-L complex for the extraction spectrophotometric determination of Fe (II) are shown in Table 1.Based on the equations of the calibration plots, the limit of photometric detection (LOD) and the limit of quantitative determination (LOQ) of iron in the form of Fe-L were calculated.

Determination of iron in soils

The accuracy and reliability of the proposed procedure was evaluated by determining iron in three standard soil samples. The analysis results (table 4) are in good agreement with certified values. The relative standard deviation (RSD) was below 3.1%.

Table 4: Determined and reference iron contents in soil samples ($n = 3$)

Sample	Iron content, %		RSD%
	Certified	**Proposed method**	
Soil 1:PS-1, COOMET № 0001-1999 BG, SOD № 310a-98	2.78±0.17	2.7	3.1
Soil 2: PS-2, COOMET № 0002-1999 BG, SOD № 311a-98	2.86±0.13	2.9	2.8
Soil 3: PS-3, COOMET № 0003-1999 BG, SOD № 312a-98	3.19±0.17	2.3	2.5

Conclusion

Spectrophotometric methods were used to study the complexation of iron (III) with 2- (piperidinomethyl) -4-methylphenol. It was found that the complex compound is formed in a slightly acidic medium (pH opt 3.8-5.2). The molar absorption coefficient is $\varepsilon_{535} = 3.29 \times 10^4$. The yield of the complex is maximum at a concentration of 4.5×10^{-4} mol / L. The complexing form of iron is $FeOH^{2+}$. The ratio of components in the complex is 1: 2. The stability constants ($\beta k = 9.5$) are calculated from the intersection of the curves. With a single extraction with chloroform, 98.4% of the iron is recovered as a complex. The accuracy and reliability of the proposed procedure was evaluated by determining iron in three standard soil samples. The analysis results (table 3) are in good agreement with certified values. The relative standard deviation (RSD) was below 3.1%.

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None.

Conflcit of Interest
The author declares no conflict of interest.

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